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(54) Title: SLOWLY DIGESTIBLE CARBOHYDRATE MATERIALS FOR USE IN FOOD AND DRINK COMPOSITIONS

(57) Abstract: Use of a carbohydrate material comprising a glycosidic backbone of which at least 5% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages as a food and/or drink ingredient which, when subjected to hydrolysis in the presence of intestinal enzymes, undergoes hydrolysis at a rate which is not greater than 0.8 times the hydrolysis rate of maltose under the same conditions such that low levels of glucose are released over prolonged periods of time. This carbohydrate material is incorporated in food and drink compositions at 15% or more by weight based on the total weight of the composition.



**WO 2004/023891 A1**

**SLOWLY DIGESTIBLE CARBOHYDRATE MATERIALS**  
**FOR USE IN FOOD AND DRINK COMPOSITIONS**

The present invention relates to the use of certain specified carbohydrate materials in food and drink compositions and to food and drink compositions containing the specified carbohydrate materials.

It is common knowledge that oligomers of glucose that are aligned to each other by an  $\alpha$ -1,4- glucosidic bond are easily hydrolysed and digested in the first parts of the digestion channel (mouth-stomach-small intestine) of humans and animals. Classical examples of such compounds are the commercially available hydrolysis products of starch, for example maltose and maltodextrins. These compounds give a rapid increase in glucose blood level after oral ingestion similar to glucose itself. Maltose is a disaccharide composed of two anhydroglucopyranoside units connected to each other by an O- $\alpha$ -1,4- linkage.

Maltodextrins are hydrolysis products of starch having a dextrose equivalent (D.E.) lower than 20. The term dextrose equivalent indicates the percentage of reducing sugars, expressed as glucose on dry basis.

U.S. Patent 2,983,613 describes the addition of dextran to bread doughs to improve the softness and shelf-life of the baked bread. The dextran may, according to this document, be used in doughs in amounts equal to from about 0.01 to about 10% by weight, based on the weight of the flour content of the dough, although it is stated that there is no advantage in employing more than 5% by weight.

The specified carbohydrate material is defined as a carbohydrate material which provides a slower release and, therefore, a slower absorption into the body, of glucose during the transit through the small intestine as compared to maltose.

Applications of the specified carbohydrate material are manifold, i.e. they can be used to deliver to the diabetic patient sufficient carbohydrates without a significant raise of the serum glucose level. Also, the addition of the specified carbohydrate material to the diet of elderly people confronted with a reduced glucose tolerance could have a beneficial effect.

In the domain of sports nutrition, the specified carbohydrate material could have interesting applications. The carbohydrate material could supply an athlete with a steady and constant carbohydrate supply during physical exercise. It could also be used in foods and/or supplements for growing children and in so called "energy drinks".

The present invention is based on the discovery that a certain amount of  $\alpha$ -1,6-D-glucopyranosidic linkages are to be used as the carbohydrate materials. According to the invention, the carbohydrate material comprises a glycosidic backbone of which at least 5% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages. Preferably, at least 10% of the glycosidic backbone in the carbohydrate material consists of  $\alpha$ -1,6-D-glucopyranosidic linkages. In a more preferred embodiment, at least 30% of the glycosidic backbone in the carbohydrate material consists of  $\alpha$ -1,6-D-glucopyranosidic linkages.

According to a first aspect, the invention provides the use of a carbohydrate material comprising a glycosidic backbone of which at least 5% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages as a food and/or drink ingredient which, when subjected to hydrolysis in the presence of intestinal enzymes, undergoes hydrolysis at a rate which is not greater than 0.8 times the hydrolysis rate of maltose under the same conditions such that low levels of glucose are released over prolonged periods of time.

More preferably, the carbohydrate material, when subjected to hydrolysis in the presence of intestinal enzymes for a period of time not exceeding 6 hours undergoes

hydrolysis at a rate which is in the range of from 0.1 to 0.6 times the hydrolysis rate of maltose under the same hydrolysing conditions.

The carbohydrate material preferably comprises at least one oligosaccharide or polysaccharide having a molecular weight in the range of from 300 to 1,000,000 daltons. The carbohydrate material may comprise one oligosaccharide or polysaccharide or may comprise a mixture of two or more oligosaccharides or polysaccharides. As stated above, the carbohydrate material comprises a glycosidic backbone of which at least 5% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages.

In the case where the carbohydrate material comprises a mixture of two or more different oligosaccharides or polysaccharides, 5% of the total glycosidic backbone components in the mixture should comprise  $\alpha$ -1,6-D-glucopyranosidic linkages. According to a preferred embodiment of the invention, the carbohydrate material is selected from isomaltose, dextrans, pullulans, alternans and mixtures of two or more of these. According to a more preferred embodiment, the carbohydrate material comprises a mixture of isomaltose and one or more of a dextran, pullulan or alternan.

A dextran is a polyglucose and dextrans of a wide variety of molecular weights and structures have been known for many years. The dextran produced by *Leuconostoc mesenteroides* NRRL B-512F has about 95% of  $\alpha$ -1,6- linkages, the other 5% being  $\alpha$ -1,3- linkages and make up the branches. Examples of dextrans that may be used according to the invention include synthetic dextrans and native dextrans such as those produced by *Leuconostoc mesenteroides* NRRL B-742, one with 14%  $\alpha$ -1,4- branch linkages and 86%  $\alpha$ -1,6- linkages and a dextran with 50%  $\alpha$ -1,3- branch linkages and the remainder being  $\alpha$ -1,6- linkages. Other examples are dextrans produced by *L. mesenteroides* NRRL B-1355. This *Leuconostoc* strain produces two polysaccharide types: a dextran with 95%  $\alpha$ -1,6- linkages in the main chain and 5%  $\alpha$ -1,3- branched linkages and another composed of alternating  $\alpha$ -1,6- linkages and  $\alpha$ -1,3- linkages in the main glycosidic chain and has 11%  $\alpha$ -1,3- branched linkages. Another example is the water soluble dextran produced by

*Streptococcus mutans* 6715 which is composed of 64%  $\alpha$ -1,6- linkages in the main glycosidic chain and 36%  $\alpha$ -1,3- branched linkages. Yet another example is the dextran produced by *Gluconobacter oxidans* ATCC 11894 which has 90%  $\alpha$ -1,6- linkages, the remaining being  $\alpha$ -1,4- linkages.

The carbohydrate material may comprise a pullulan. Pullulan is a viscous polysaccharide that may be extracellularly produced by growing certain yeasts on sugars and comprises a polymer of D-glucopyranose residues, containing  $\alpha$ -1,4- linkages and  $\alpha$ -1,6- linkages in the ratio 2:1. The structure is that of a polymer of maltotriose, connected end-to-end by an  $\alpha$ -1,6- glycosidic linkage. In addition to maltotriose units, pullulan also has 5 to 7% maltotetraose units distributed along the main chain. Thus, about 33% of the glycosidic linkages in pullulan are  $\alpha$ -1,6- linkages, the remainder being  $\alpha$ -1,4- linkages.

Alternatively, the carbohydrate material may be, or comprise, an alternan. Alternan is a homopolymer of glucose and has alternating  $\alpha$ -1,6- and  $\alpha$ -1,3- linked glucose residues in the main chain with varying amounts of  $\alpha$ -1,3- branch linkages.

The present invention also provides a food or drink composition which contains as one of its components the carbohydrate material as described above in an amount greater than 15% by weight based on the total weight of the composition. Typically, the food or drink composition may be a diabetic food or drink, a baby food or drink, a diet food or drink, for instance for sedentary people, a specially formulated food or for people having a reduced glucose tolerance, for instance the elderly, or a food or drink for growing children. The carbohydrate material may, advantageously, be used as a component in sports or energy beverages. Typically, the carbohydrate material will be present in a composition in an amount of at least 20% by weight.

The presence of the carbohydrate material in food and drink compositions provides, as mentioned earlier, a slower release, and therefore a slower absorption into the body, of glucose. This is correlated with a low glycemic index. Accordingly,

the present invention further provides the use of a carbohydrate material comprising a glycosidic backbone of which at least 5%, preferably at least 10% and more preferably at least 30%, consists of  $\alpha$ -1,6-D-glucopyranosidic linkages in the manufacture of food and drink compositions having a low glycemic index. It follows that it is possible to reduce the glycemic index of a food or drink composition by replacing at least part of the carbohydrate content thereof with a slowly digestible carbohydrate material comprising a glycosidic backbone of which at least 5% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages, as disclosed herein before.

**Example 1: In-vitro hydrolysis of maltose and isomaltose by rat intestinal acetone powder**

A 1% substrate solution (w/w) of maltose or isomaltose was prepared in 0.05 M phosphate buffer pH 6 and equilibrated at 37°C for 10 minutes. A suspension of 2.5% rat intestinal acetone powder (Sigma) was used as a source of glucoamylase-maltase complex and sucrase-isomaltase and was prepared in 0.05M phosphate buffer pH 6 and equilibrated at 37°C for 10 minutes. 0.6ml rat intestinal acetone powder (excess) was added to 6 ml of substrate solution and mixed. The mixture was incubated at 37°C and a 1.5 ml sample was taken (0 hours incubation time). Further samples were taken after 2, 4 and 6 hours of incubation. The samples were diluted with 4 ml of demineralised water and boiled for 5 minutes. After the denaturation step, each sample was filtered through a 0.45  $\mu$ m filter.

The filtrate was sent through a Dionex OnGuard-ATM filter. Glucose was determined by HPLC. The results for the in-vitro small intestinal digestion tests for maltose and isomaltose are given in Table 1.

**Table 1**In vitro hydrolysis of maltose and isomaltose by rat intestinal acetone powder

| Compound   | % glucose produced |         |         |
|------------|--------------------|---------|---------|
|            | 2 Hours            | 4 Hours | 6 Hours |
| Maltose    | 100.0              | 100.0   | 100.0   |
| Isomaltose | 49.0               | 52.0    | 58.0    |

This example shows the hydrolysis kinetics of isomaltose. This example shows a slower release of glucose compared to maltose.

**Example 2: In-vitro hydrolysis of dextrans by rat intestinal acetone powder**

The same experimental procedure as in Example 1 was followed, except that the 2.5% rat intestinal acetone powder solution was replaced by a 10% rat intestinal acetone powder solution. Dextrans of different molecular weight were used as substrates. Dextrans with Mw ~1000, ~5000, ~12000, ~25000, ~50000, ~80000, ~150000 and ~270000 were from Fluka. The dextrans T-500 (Mw~500000) and T-2000 (Mw~2000000) were from Amersham Pharmacia Biotech. The results are presented in Table 2.

**Table 2**

| Compound                | % glucose produced |         |         |
|-------------------------|--------------------|---------|---------|
|                         | 2 Hours            | 4 Hours | 6 Hours |
| Maltose                 | 100.0              | 100.0   | 100.0   |
| Isomaltose              | 61.1               | 75.5    | 84.5    |
| Dextran 1000            | 38.9               | 54.0    | 64.4    |
| Dextran 5000            | 34.3               | 46.7    | 55.0    |
| Dextran 12000           | 24.8               | 33.5    | 39.5    |
| Dextran 25000           | 18.6               | 25.4    | 30.1    |
| Dextran 50000           | 15.4               | 20.8    | 24.9    |
| Dextran 80000           | 14.5               | 19.0    | 22.3    |
| Dextran 150000          | 12.3               | 17.2    | 20.6    |
| Dextran 270000          | 11.8               | 16.9    | 20.2    |
| Dextran T 500 Pharmacia | 12.7               | 17.9    | 20.3    |
| Dextran T2000 Pharmacia | 11.8               | 16.3    | 19.0    |

This example shows the hydrolysis kinetics of a series of dextran polymers having different degrees of polymerisation. This example shows a slower release of glucose compared to maltose.

**Example 3: In-vitro hydrolysis of pullulans by rat intestinal acetone powder**

The same experimental procedure as in Example 2 was followed. Pullulans with Mw ~5000, ~10000, ~20000, ~50000, ~100000, ~200000, ~400000, ~800000 from Shodex and isomaltose were used as substrates. The results are presented in Table 3.

**Table 3**

| Compound   | % glucose produced |         |         |
|------------|--------------------|---------|---------|
|            | 2 Hours            | 4 Hours | 6 Hours |
| Maltose    | 100.0              | 100.0   | 100.0   |
| Isomaltose | 65.7               | 79.1    | 87.5    |
| P-5        | 44.2               | 57.5    | 70.4    |
| P-10       | 26.9               | 37.1    | 46.0    |
| P-20       | 18.8               | 26.0    | 32.8    |
| P-50       | 13.3               | 18.6    | 23.3    |
| P-100      | 10.1               | 14.6    | 18.5    |
| P-200      | 8.6                | 12.6    | 16.6    |
| P-400      | 8.0                | 11.7    | 15.1    |
| P-800      | 7.7                | 11.5    | 14.6    |

This example shows the hydrolysis kinetics of a series of pullulan polymers having different degrees of polymerisation. The example shows a slower release of glucose compared to maltose.



**Example 4: Sport or isotonic drink composition****Ingredients for one litre of drink:**

|                          |              |
|--------------------------|--------------|
| Carbohydrate Material*   | 30g          |
| Sucrose                  | 40g          |
| Sodium chloride          | 1.27g        |
| Citric acid              | 1g           |
| Orange flavour           | 2g           |
| Sodium benzoate (10%w/v) | 1.5ml        |
| Water                    | to one litre |

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\* Any carbohydrate material comprising a glycosidic backbone of which at least 5% comprises a  $\alpha$ -1,6-D-glucopyranosidic linkages.

For the preparation of the drink, the sucrose and the carbohydrate material were dissolved into water and then all other ingredients were added to the solution obtained.

**Example 5: Cereal bar formulation and method of manufacture**

|                           |                 |
|---------------------------|-----------------|
| <b><u>Ingredients</u></b> | <b><u>%</u></b> |
| Cereal flakes             | 30              |
| Carbohydrate material     | 20              |
| Rice crispies             | 8               |
| Raisins                   | 5               |
| Binding syrup (see below) | 37              |

|   |                 |
|---|-----------------|
| <b><u>Binding syrup formulation</u></b> | <b><u>%</u></b> |
| Glucose syrup (9% fructose)             | 27.9            |
| Sucrose                                 | 15.2            |
| Maltodextrin (6DE)                      | 13.7            |
| Invert sugar                            | 12.9            |
| Glycerol                                | 10.8            |
| Margarine                               | 7.8             |

|                |           |
|----------------|-----------|
| Sorbitol syrup | 3         |
| Lecithin       | 2.6       |
| Water          | 4.8       |
| Salt           | 1.3       |
| Vanilla        | as needed |

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\* Any carbohydrate material comprising a glycosidic backbone of which at least 5% comprises a  $\alpha$ -1,6-D-glucopyranosidic linkages.

#### Manufacturing process of cereal bars

The ingredients of the binding syrup were blended and to this blend was added the carbohydrate material. The mixture was then heated to 100°C. A blend of the remaining ingredients (cereal flakes, rice crispies and raisins) was prepared. The binding syrup was then added and mixed with the other ingredients until a uniform mixture was obtained. The mixture was then formed into bars and packaged.

## CLAIMS

1. Use of a carbohydrate material comprising a glycosidic backbone of which at least 5% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages as a food and/or drink ingredient which, when subjected to hydrolysis in the presence of intestinal enzymes, undergoes hydrolysis at a rate which is not greater than 0.8 times the hydrolysis rate of maltose under the same conditions such that low levels of glucose are released over prolonged periods of time.
2. Use according to claim 1, characterised in that the carbohydrate material, when subjected to hydrolysis in the presence of intestinal enzymes for not greater than 6 hours, undergoes hydrolysis at a rate which is in the range of from 0.1 to 0.6 times the hydrolysis rate of maltose under the same conditions.
3. Use according to either claim 1 or claim 2, characterised in that the intestinal enzymes are selected from glucoamylase-maltase, sucrase-isomaltase and mixtures thereof.
4. Use according to any one of claims 1 to 3, characterised in that the carbohydrate material comprises a glycosidic backbone of which at least 10% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages.
5. Use according to claim 4, characterised in that the carbohydrate material comprises a glycosidic backbone of which at least 30% consists of  $\alpha$ -1,6-D-glucopyranosidic linkages.
6. Use according to any one of claims 1 to 5, characterised in that the carbohydrate material comprises at least one oligosaccharide, polysaccharide or mixtures thereof having a molecular weight in the range of from 300 to 1,000,000 daltons.

7. Use according to claim 6, characterised in that the carbohydrate material is selected from isomaltose, dextrans, pullulans, alternans and mixtures of two or more of these.
8. Use according to any one of claims 1 to 7, as an ingredient for diabetic foods, baby foods, special dietary formulations and/or sports drinks.
9. Use according to any one of claims 1 to 8, characterised in that the carbohydrate material is added in amounts of at least 15% by weight to said food and/or drink compositions.
10. Use according to claim 9, characterised in that the carbohydrate material is added in amounts of at least 20% by weight to said food and/or drink compositions.

# INTERNATIONAL SEARCH REPORT

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## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A23L1/054 A23L1/308

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal, BIOSIS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### \* Special categories of cited documents :

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# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages   | Relevant to claim No. |
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